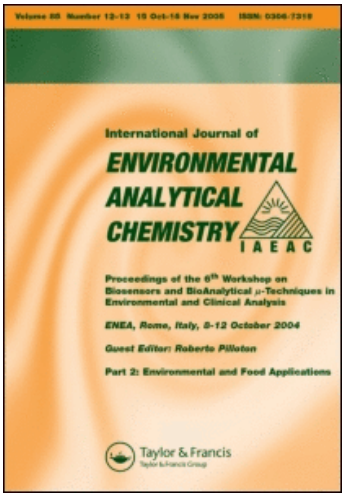

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Determination of Fluorine in Vegetation by Proton Activation Analysis

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Techniques have been developed for proton activation analysis using the $^{19}F(p,p'\gamma)^{19}F$ reaction to measure the fluorine content of pulverized samples of vegetation which have been exposed to fluorides in the atmosphere or soil. The method is non-destructive and neither the chemical form of fluorine in the sample nor the type of vegetation analyzed appears to affect results. Calibration is performed by analyzing samples to which known amounts of fluorine are added. The fluorine content of 11 vegetation samples was determined by proton activation analysis and by standard chemical techniques. The values obtained by the two methods were in generally good agreement. Fluorine concentrations greater than 1 ppm can be measured with uncertainties ranging from about 50% at 5 ppm to less than 10% at concentrations above 50 ppm.

INTRODUCTION

This report describes the development of techniques for the measurement of fluorine in the leaves of plants by proton activation analysis. Fluorine enters the environment from numerous man-made and natural sources and accumulates in vegetation after uptake either from the soil or from polluted atmospheres. Selective, accurate and sensitive analytical techniques are needed to measure the fluorine content of plant and animal tissues.[1]

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Fluorine, usually in the form of inorganic fluorides, is produced during the combustion of coal for electricity, heating of ore in the production of aluminum and steel, and during the manufacture of fertilizer and glass. Vegetation avidly absorbs fluorine from the atmosphere and from soil under certain conditions and ingestion of fluoride-contaminated foliage by foraging animals can lead to bone disease and other metabolic disorders.[2,3] Plant and animal foods which contain fluorine are also an important part of the human diet.[4,5,6] Unfortunately, existing chemical methods of fluorine analysis have serious deficiencies, particularly when estimates are made of total dietary intake.[1]

Chemical methods for the analysis of fluorine frequently are affected by the chemical form of fluorine and the chemical or physical nature of the sample. Sample preparation procedures are time-consuming and subject to random and systematic errors either due to loss of fluorine or contamination with extraneous fluorine.[7] Separation techniques, required before fluorine can be analyzed accurately by chemical methods, also are subject to systematic and random errors. Activation analysis, in principle, does not require extensive sample preparation or purification procedures[8–10] and precise measurements can be made directly on dry, powdered samples without danger of contamination or loss of fluorine.

Activation of fluorine can be induced by a variety of projectiles.[11] In this study, we chose the $^{19}F(p,p'\gamma)^{19}F$ reaction[8,10] because it possesses several useful qualities. Bombardment of fluorine with low energy protons (< 3 MeV) produces γ rays of 110 and 197 keV which can be readily detected with Ge(Li) γ ray detectors of modest cost. The resulting measurements appear to be at least as sensitive and precise as current chemical techniques, are not affected by the chemical form of fluorine, and the method is amenable to improvements which should make possible accurate determinations of total dietary intake of fluorine.

METHODS

Preliminary work was performed to evaluate the excitation curves for the production of 110 and 197 keV γ rays using a thick target of CaF_2 (Figure 1). Although the cross-sections for these two γ rays are about equal, we chose the 197 keV line because the background under the line rises more slowly with energy. We selected an energy of 2.15 MeV, the highest energy within the stable operating range of the Van de Graaff accelerator available to us, because the sensitivity and accuracy of fluorine determination is greater at higher bombarding energies. At this energy, the cross-section does not change rapidly and fluctuations in machine energy are not important.

Samples for analysis were prepared in a very simple way. Dried and pulverized vegetation was placed in a die with a diameter of 3 cm and compressed with pressures ranging up to 400 bar. A flat and relatively strong disc with a thickness of several mm was obtained. An effort was made to minimize absorption of water during the pressing and subsequent transfer

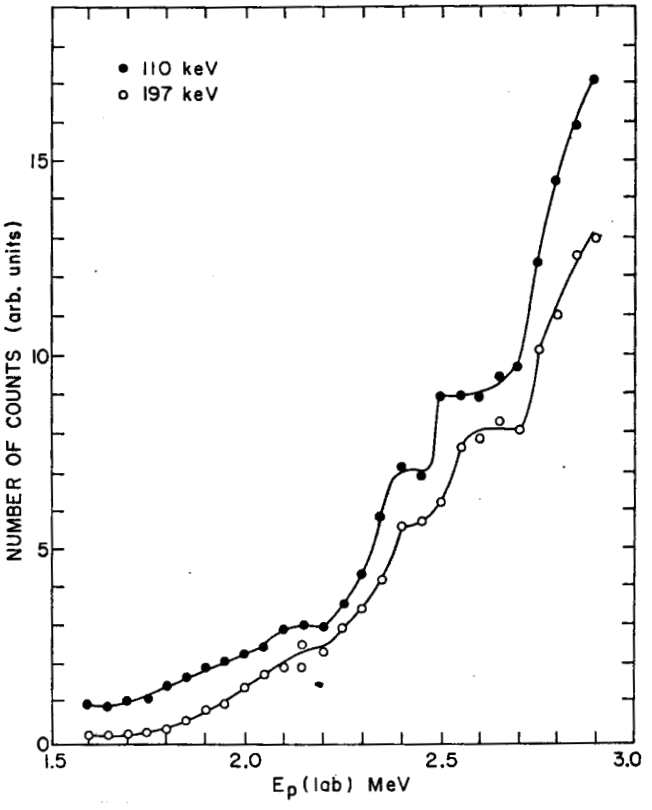

FIGURE 1 Excitation curve for the 110 and 197 keV γ rays produced in the $^{19}F(p,p'\gamma)^{19}F$ reaction using a thick target of CaF_2. The statistical uncertainties are less than the size of the data points.

to the bombardment chamber. The total amount of material used was 1–2 grams, but this could be reduced by about an order of magnitude.

The sample was mounted on an insulated target chamber attached to a "target wobbler".[12] This device moved the collimated beam spot of 2 mm diameter over the face of the sample in a Lissajous pattern of 1 cm^2 area. This was advantageous for two reasons. First, a large fraction of the material

was sampled and possible sample inhomogeneities were eliminated. Second, the heat dissipation produced by the beam stopping in a given target element was greatly reduced, an important factor in samples containing organic matter. We found that the conductivity of these samples was high enough to give reliable current integration.

The 197 keV γ rays were detected with a 20 cm^3 coaxial Ge(Li) γ ray detector. Energy resolution was 1.8 keV at 197 keV γ ray energy. The distance from the front face of the target to the detector was 20 mm which was constant to ± 1 mm from sample to sample. This variation resulted in an uncertainty of $\pm 10\%$ in the yield determinations which is generally the major source of uncertainty in this work. This uncertainty can be eliminated easily by better design of the sample holder.

Analysis times were generally one hour or less with a beam current of 15 nA. At this level there was little or no evidence of damage to the targets and tests with beam currents up to 60 nA indicated only a slight ($< 10\%$) dependence of yield on beam current. At 15 nA the yields were reproducible over extended periods of measurement with a single target. Permissible beam currents could be substantially increased by cooling the target to liquid nitrogen temperature or by use of convection cooling in a gas atmosphere. Exposure of samples at higher beam currents or for longer periods of time also would reduce the statistical uncertainty of the measurement.

No attempt was made to make an absolute measurement of the fluorine concentration. Instead, measurements were made on two aliquots of a sample of vegetation, one with and one without the addition of sodium fluoride to a concentration of 200 ppm. The amount of endogenous fluorine was deduced from the ratio of the two measurements. We also investigated the possibility that a single calibration curve could be constructed which would apply to all samples of vegetation. This rests on the assumption that the stopping powers of the various substances are the same. Fluorine was added to gladiolus and corn leaf samples containing negligible endogenous fluorine to give concentrations of 41, 62, and 134 ppm. The production of the 197 keV γ rays was found to be a linear function of the fluorine content of the calibration sample with no dependence on substance within the accuracy of the measurements. This is demonstrated by the curve shown in Fig. 2.

RESULTS

We measured the fluorine content of eleven samples of vegetation by the techniques described above and used the calibration curve in Figure 2 to convert the measured gamma ray yield to parts per million fluoride (μg per gram dry weight). The results are given in Table I along with results obtained

by chemical analyses.[13] Good correspondence was obtained between fluorine analyses by the two methods with the exception of the alfalfa and grass sample.

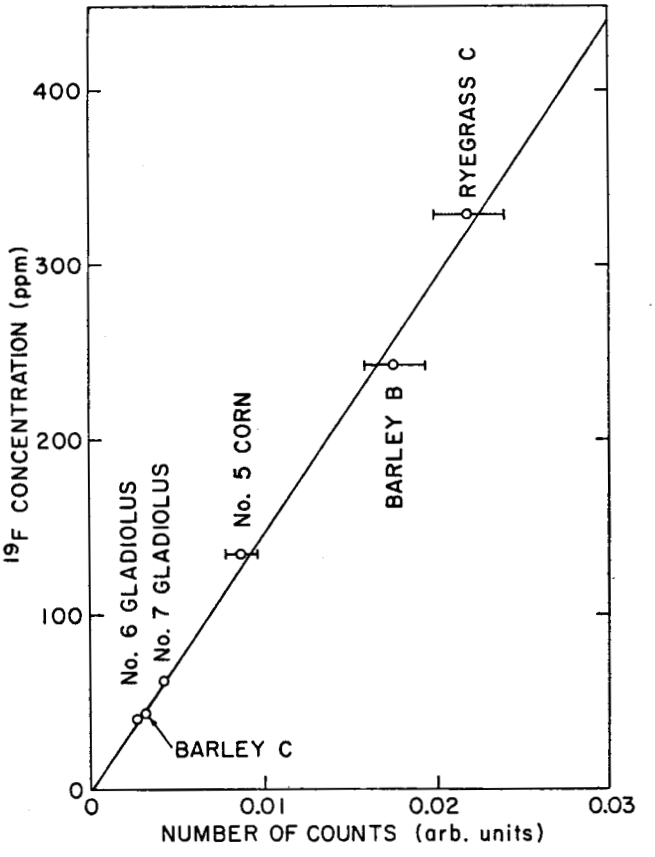

FIGURE 2 Calibration curve for determination of fluorine concentrations by proton activation analysis. Calibration materials were obtained by adding known amounts of fluorine to samples with very low fluorine content. The curve relates the known fluorine content of the various targets to the experimentally determined counting rate for the ^{19}F 197 keV γ ray.

Dependence of the results on target composition was checked by measuring three samples of alfalfa: normal, ashed and ashed containing 35% CaO. The composition of the sample did not appear to affect the measurements. No tests were made on the ashed samples for dependence on beam current,

but they should be more resistant to decomposition than materials containing organic matter.

DISCUSSION

In one of the samples analyzed, alfalfa and grass (line 4, Table I), proton activation analysis gave substantially higher results than chemical analysis.

TABLE I

Comparison of fluoride measurements by proton activation and chemical analyses

Sample	Fluorine content (ppm by weight) Proton activation analysis†	Chemical analysis‡
Rye Grass	330	370±37
Barley	43	51± 5
Alfalfa	6±3	6± 5
Alfalfa and Grass	657	409±41
Alfalfa	66	55± 6
Ashed Alfalfa	58	55± 6
Ashed Alfalfa+Ca0	65	55± 6
Apple	83	75± 8
Cotton	511	490±49
Orchard Grass	40	33± 5
Pasture Grass	37	28± 5

†The values for rye grass and barley were found by comparison of samples with and without known amounts of added fluorine. The other values were found by using the calibration curve in Fig. 2. The uncertainties are $\sim \pm 10\%$ due to variations in geometry except for the sample of alfalfa (line 3) where the uncertainty is statistical.

‡The uncertainties quoted are standard deviations taken from previous studies.

Individual samples of vegetation may contain fluorine in a form inimical to accurate chemical analysis. These errors may not have been detected previously because the absolute accuracy of chemical methods has been estimated only by indirect means. Proton activation analysis should be useful in identifying such samples because it provides an independent check on fluorine content.

Activation analysis offers several advantages over standard chemical techniques. The sample is not destroyed and may be used to measure other components. There is no blank value and little opportunity for either loss

of fluorine or contamination. The technique is relatively straightforward and results are not affected by the chemical nature of fluorine.

Although this work demonstrates that proton activation analysis has considerable promise for solving problems relating to fluorine accumulation, it is not likely to become a routine method in analytical laboratories because the equipment for inducing proton emissions is available only at a few locations. However, improvements in sensitivity and accuracy suggested by this work indicate that the method may be suitable as a non-chemical validation procedure for fluorine analyses and may provide more accurate data on the total dietary intake of fluorine.

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